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AN INTRODUCTION TO LITHIUM BATTERIES

W.N.C. Garrard

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AN INTRODUCTION TO LITHIUM BATTERIES

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ABSTRACT

Lithium batteries are being introduced into all three services in the Australian Defence Force. However, general information concerning lithium batteries is not available in a condensed form. This review examines various aspects of lithium batteries, including battery technology, safety aspects, purchasing, packaging, transport, storage and disposal.

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AN INTRODUCTION TO LITHIUM BATTERIES

1. INTRODUCTION

Lithium batteries are rapidly gaining acceptance with the Australian Defence Force since they offer a number of advantages over other conventional battery systems. These include a high voltage per cell, high energy density, flat discharge characteristics, excellent shelf-life, and a wide operational temperature range. Such batteries also have disadvantages, principally their cost, safety risks, and voltage delay.

It is the aim of this report to outline the hazards associated with primary lithium batteries so as to minimise the possibility of an accident. Attention is directed at the safety, transport, storage, and disposal of lithium batteries. The information presented in this report is very general and any specific questions concerning these batteries should be directed to this laboratory.

Before discussing the risks associated with these batteries a brief summary of this technology will be presented. Note: a cell is a device which generates electricity, while a battery is a collection of two or more cells (e.g. a 12 V lead-acid battery consists of six lead-acid cells).

2. BATTERY TECHNOLOGY

2.1 General construction

Lithium cells use non-aqueous solvents for the electrolyte solvent, as lithium reacts with water. Electrolytes may be organic (for example, acetonitrile or propylene carbonate) or inorganic solvents (for example, sulphur dioxide or thionyl chloride) containing a suitable solute to provide electrical conduction. Lithium also reacts with these electrolyte solvents, however, as the reaction proceeds it produces a film on the

lithium surface which inhibits further reaction. It is this protective film on the lithium surface that gives rise to the voltage delay problem and excellent shelf-life associated with these batteries.

Lithium foil acts as the anode in these cells. The anode reaction is the same in all lithium cells, that is, the oxidation of lithium metal to lithium ions. The cathode material and reaction are dependent upon the type of cell under consideration. In lithium-sulphur dioxide cells, for example, the cathode material is a teflon-carbon black mixture supported on an expanded aluminium or nickel grid and the cathode reaction involves the consumption of sulphur dioxide. Other popular cathode materials include thionyl chloride, carbon monofluoride, manganese dioxide, copper sulphide, or ferrous sulphide. Anode and cathode are generally isolated from each other by a porous separator. Books by Linden [1], Gabano [2], and Venkatasetty [3] as well as manufacturers' technical data sheets contain more detailed information concerning the construction details, chemistry, and performance of lithium batteries.

2.2 Battery Classes

Because there is a wide range of available electrolytes and cathode materials there are many batteries that are classified as 'lithium batteries'. However, each 'lithium battery' may be classified as belonging to one of the following general categories: soluble cathode cells, solid cathode cells, and solid electrolyte cells.

2.2.1 Soluble Cathode Cells

These cells/batteries use cathode materials which are gases (sulphur dioxide) or liquids (thionyl chloride) at room temperature. Cells in this category are manufactured in many different configurations with wide range of capacity. Cylindrical configurations are used for the smaller capacity types (up to ca. 25 Ah), while higher capacity cells use flat parallel plates housed in prismatic containers. These cells are used in applications requiring low to high discharge rates. Key characteristics include high energy and power output, low temperature operation, and long shelf-life.

2.2.2 Solid Cathode Cells

This battery type uses solid materials for the cathode as opposed to liquid or gaseous materials. Section 2.1 contains a partial list of solid cathode reagents. Solid cathode cells do not possess the high discharge rates that are associated with the soluble cathode systems. Button and cylindrical configurations are available for low to medium rate applications such as memory backup, watches, calculators, etc. High energy output at moderate rates and non-pressurised construction are key characteristics of this family.

2.2.3 Solid Electrolyte Cells

Cells from this category have an extremely long storage life, but a very low discharge rate (microamperes). Thus these cells are used in applications such as memory backup and cardiac pacemakers. Iodine is the cathode material used in commercial

cells. Excellent shelf-life, no leakage, and long-term microampere discharge rates are their main characteristics.

3. SAFETY ASPECTS

The remainder of this report will mainly be concerned with lithium-sulphur dioxide and lithium-thionyl chloride batteries, because such batteries pose the greatest risks with respect to safety. Although solid cathode and solid state batteries are generally considered to be not as dangerous as liquid cathode cells, the following information should be assumed to apply to all lithium batteries unless stated in this report or in technical information supplied by manufacturers.

Under no circumstances should lithium batteries be used in equipment not designed to operate with such batteries, nor should one type of lithium battery be substituted with another. The failure rate for lithium-sulphur dioxide batteries is very low: in the U.S. between 1977 and 1981 only 21 failures (19 of which could be traced to misuse or abuse) were reported after delivery of 568000 batteries (i.e. 0.0037% failure rate) [4].

3.1 Abuse and Safety Devices

Lithium batteries are quite safe when used under normal conditions, but abuse may result in explosions, fires, and the liberation of toxic substances. Fires arise from interaction of lithium with its environment. Lithium burns when exposed to oxygen at elevated temperatures. The presence of hydrogen, produced when lithium reacts with water, can lead to fires or explosions. Moreover, the organic electrolyte solvents are generally flammable. Explosions and venting are a result of pressure build up in the battery. It has been calculated [5] that a 'D' size lithium-sulphur dioxide cell is approximately equivalent to 40 g of TNT.

Overheating is the major cause of the above effects. High discharge rates, external and internal short circuits, forced over-discharge, attempted charging, and externally applied heat (fire) all result in the battery overheating. Physical damage, such as manufacturing defects (for example, corrosion of the container and higher than usual internal resistance) , or the puncturing and crushing of cells is another source of abuse. Such hazardous conditions should not arise if (a) the batteries are operated within the specification ranges set down by the manufacturer, (b) users are warned of the hazards, (c) a large warning label is attached to the battery, and (d) protective devices are built into either the equipment or the battery.

Diodes, fuses, and thermal cutouts are used to minimise the effects of electrical abuse. Diodes are used to negate attempts to over-discharge or recharge batteries, whether via an external source or internally by cells connected in parallel. Fuses are fitted to batteries to protect against high discharge rates or short circuits. Finally, thermal cutouts (i.e. thermostats or polyswitches) ensure that the internal temperature of the battery does not rise above a preset value. Placement of the thermal cutouts is important. Almost all large batteries have these protective devices fitted internally, while smaller batteries may have none, one, or more of the devices

contained within the outer casing. In the case where batteries do not possess any in-built safety devices the user should consult the battery or equipment manufacturer's literature to ascertain which safety devices should be installed by the end user.

Mechanical safety devices further reduce the effects of abuse. This device is usually a safety vent in the cell case that will actuate when the internal pressure rises above a certain value (ca. 200 to 400 psi depending on the manufacturer). Venting causes the electrolyte to be expelled from the cell, thus making the battery inoperative. Such vents therefore reduce the probability that a battery will explode. Batteries which have vented require special disposal procedures (see section 8). Further information is contained in the specifications [6 - 9].

3.2 Personal Safety

Lithium batteries may be subjected to normal handling, but users should be informed of the dangers in attempting to open, crush, incinerate, or recharge the batteries. Batteries which appear to be disfigured or leaking should be disposed of promptly (see section 8). Personnel disposing of faulty batteries must wear rubber gloves, apron, and a face-shield. Respirators or gas masks may be required if the battery is leaking and a safe distance should be maintained from any battery which feels hot. The battery should be removed only after it cools. In confined spaces, on detecting a toxic gas, the area should be vacated immediately. Dispose of the battery only after the gas has dispersed.

3.3 Firefighting

Although graphite powder extinguishers are recommended for lithium fires, they are only effective during the early stages. If graphite powder is used the extinguished residue should be washed with excess water to destroy any remaining lithium. Carbon dioxide extinguishers are ineffective in extinguishing lithium fires, while Halon extinguishers must not be used. A fine water spray is the most effective way to combat a lithium battery fire. The spray cools adjacent batteries (lowering the probability of these batteries venting or exploding), helps extinguish lithium fires, destroys any lithium, and absorbs toxic gases. Further information is contained in section 7 and references 6, 7, 10, and 11.

3.4 Chemical Hazards

It is of interest to examine the hazards associated with the chemicals, both reactants and products as well as electrolytes, in lithium cells. More information is contained in Sax's book [12].

3.4.1 Reactants

Lithium is an alkali metal with a melting point (m.p.) of 180 C. It reacts slowly with water to produce an alkaline solution and hydrogen. The resulting solution is corrosive, while hydrogen is a potential explosive. Lithium may affect the kidneys if ingested.

Sulphur dioxide is a colourless, suffocating gas with a m.p. of -72 C and a boiling point (b.p.) of -10 C. It reacts with water (vapour or liquid) to form sulphurous acid, a mildly corrosive substance. Sulphur dioxide is intensely irrita[illegible]g to the eyes and respiratory tract. Thionyl chloride is a colourless liquid with a suffoc[illegible]ing odour. Its m.p. and b.p. are -104 and 76 C, respectively. At temperatures exceeding 140 C it decomposes to chlorine, sulphur dioxide, and sulphur chloride (a substance which is corrosive and irritating to the eyes, nose, and throat). Thionyl chloride is hydrolysed by water to give sulphur dioxide (sulphurous acid) and hydrochloric acid. The vapour and liquid are strongly irritating and corrosive to the skin, mucous membranes, and eyes. Metallic corrosion is generally more aggressive in environments containing these substances.

The chemicals present in solid cathode and solid electrolyte cells may also be dangerous. Copper sulphide and ferrous sulphide liberate hydrogen sulphide on contact with water (vapour or liquid). Exposure to 800 - 1000 ppm of hydrogen sulphide, a flammable gas, may be fatal within 30 minutes. Sulphur dioxide is liberated from sulphide compounds that are heated to high temperatures. Sulphides can react violently and explosively with oxidising agents. Manganese dioxide and chromium oxide are powerful oxidising agents; bringing these chemicals into contact with combustible material may cause a fire. Chromium oxide affects the body in a variety of ways: ingestion causes vomiting and diarrhoea, inhalation results in nasal and pulmonary irritation, while skin contact leads to irritation and ulceration.

3.4.2 Products

Sulphur, sulphur dioxide, lithium dithionite, and lithium chlori[illegible]re the products in liquid cathode cells. At temperatures exceeding 260 C, su[illegible]nites in the air to produce sulphur dioxide. Lithium chloride is not particularly da[illegible]s. However, prolonged absorption may cause disturbed electrolyte balance, impaired renal function, and central nervous system disturbances. Although lithium dithionite is known to decompose violently at elevated temperatures, no other information is currently available regarding this compound.

The products in the two remaining classes of lithium batteries include lithium fluoride, copper, lithium sulphide, and lithium iodide. Lithium fluoride is highly toxic, with two to three grams being a lethal dose. Some effects of fluoride poisoning are sclerosis of the bones, loss of weight, anaemia, and dental defects. Lithium sulphide displays the same properties as other sulphides (see above). Lithium iodide, which is dangerous only on prolonged exposure, affects the skin and mucous membranes.

3.4.3 Electrolyte

Electrolytes consist of a solvent, such as acetonitrile, dimethyl sulphoxide, dimethoxyethane, or propylene carbonate, together with a salt, for example, lithium aluminium chloride, lithium bromide, or lithium perchlorate. Most solvents are colourless, liquid in the range 0 to 100 C, and flammable (flash points range from 4.5 C for dimethoxyethane to 135 C for propylene carbonate). Acetonitrile causes skin irritation (LD/50 in rats = 3.8 g/kg). Dimethyl sulphoxide freely enters the body through the skin (LD/50 in rats > 20g/kg). It irritates the skin, induces vomiting, and has been reported to produce corneal opacities in test animals. Dimethyl sulphoxide acts to carry other agents into the body, that is, it is a very effective skin penetrant. Little is known about the toxic effects of dimethoxyethane and propylene carbonate.

All lithium salts used in the electrolyte should be treated the same as lithium chloride (section 3.4.2). Lithium perchlorate also irritates the skin and mucous membranes as well as being a powerful oxidising agent which explodes if heated.

3.4.4 Chemical Interactions

Thus far, nothing has been said about the interaction between the various compounds in the lithium cell. Lithium can react quite vigorously with acetonitrile, sulphur, sulphur dioxide, thionyl chloride and lithium dithionite. Most reactions, however, are poisoned by other components in the system. For example, the reaction between lithium and acetonitrile generates a considerable quantity of heat (thermal run away conditions), but water in trace amounts virtually stops the reaction. Reaction between sulphur dioxide or thionyl chloride and lithium is blocked by the precipitation of the reaction product on the lithium surface (see section 2.1). Alternatively, some reactions are catalysed by other cell components, for example, carbon (cathode material in some cells) accelerates the reaction between lithium and lithium dithionite.

4. PURCHASING

All lithium-sulphur dioxide or lithium-thionyl chloride batteries should meet the appropriate specifications [6, 8, 9]. The British standard [7] is a general specification for all lithium batteries. Such specifications set out the design, marking, labelling, and packaging of the batteries (see section 5); quality control during manufacture; as well as the electrical and environmental tests which these batteries must pass before being approved for use.

The design must include a description of the battery's electrical (open circuit voltage, capacity, and discharge rates), physical (weight, dimensions, protective devices, and position of protective devices), and environmemtal (ability to withstand vibration, shock, pressure and temperature variations, drop, as well as corrosion) characteristics. Marking and labelling includes the part number, manufacturer's name, year of manufacture, serial number, and a warning (on separate label) such as:

> WARNING - LITHIUM BATTERY. Do not charge, short-circuit, incinerate or mutilate this battery otherwise battery may vent or explode.

Quality control must be carried out by the manufacturer to ensure that raw materials, components, and manufacturing processes meet the requirements of the specification, and, if possible, quality control records should be available for inspection. With regard to the electrical and environmental tests, the specification must state the procedure for the sampling and testing.

5. PACKAGING

References 6, 13, 14, and 15 detail the packaging requirements for lithium batteries. Battery terminals must be insulated and each battery packed in a cardboard box to prevent short-circuiting. Each boxed battery may be further protected by heat

sealing the box in polyethylene. Several batteries (depending on the battery make) are then packed together in a large cardboard box, which may be palletised or placed in an outer cardboard box, wooden box or drum. All boxes must be labelled [13, 15] to indicate the contents (note that reference 13 groups all lithium batteries into one category based on their lithium content). Recently, MRL made a submission to the Department of Transport and Communications requesting that lithium-sulphur dioxide and lithium-thionyl chloride batteries be reclassified.

6. TRANSPORT

Provided the batteries are contained in their unit packages, there are no restrictions on the quantities of lithium batteries that may be transported by rail, road or sea. Appropriate firefighting equipment and instructions concerning the potential hazards should be issued to those responsible for the consignment.

IATA [15] places severe restrictions upon airborne transportation. It is forbidden to transport large liquid cathode batteries on passenger aircraft, however, up to 5 kg (gross) of large solid cathode batteries are permitted. Lithium batteries are excluded from these restrictions if each cell contains less than 0.5 g of lithium, and each battery contains less than 1 g (liquid cathode battery) or 2 g (solid cathode battery) of lithium. Large quantities of liquid cathode and solid cathode batteries may be transported on cargo aircraft. Discharged, partly discharged, or damaged batteries cannot be air transported. Equipment containing lithium batteries may be transported by aircraft provided the batteries meet packing instructions similar to the above, and each battery contains less than 125 g (passenger aircraft) or 500 g (cargo aircraft) of lithium. Again, firefighting equipment and instructions regarding the hazards must be issued to the person(s) in charge of the consignment. If possible, lithium batteries involved in hazardous situations should be jettisoned from the aircraft.

The above regulations may be over-ridden by military waivers. For example, the U.S. Defence Force allows the carriage of approved lithium batteries on passenger aircraft with the following provisions [16]: (a) new or partly discharged batteries without unit wrapping must be installed in equipment; (b) spare batteries must be contained in their unit wrapping so as to avoid short-circuits; (c) damaged cells will not be carried; and (d) fully discharged batteries will be carried away from forward areas as long as there are no possibilities for short-circuit. Similar waivers are under consideration by the Australian Defence Force.

7. STORAGE

The Army specification [6] presents the requirements for storage of lithium batteries. These conditions are similar to those in use overseas [10, 11]. Batteries must be stored in the unit packaging until used. It is not permissible to store fresh and discharged batteries in the same stack. The storage facility must be dry and well ventilated, with a storage temperature not exceeding 50 C (lower temperatures will prolong shelf-life). No smoking or naked flames should be permitted. Stack sizes are limited to 20 cu. m, with aisles of 3 m width between stacks and 1 m clearance on all other sides. A distance of 1 m must exist between the top of the stack and the sprinkler heads. No other commodity must be stored in the same stack, while no flammable

materials can be stored with the batteries. Firefighting equipment must be available and should include a fixed water sprinkler fire suppression system, graphite powder extinguishers, gas masks, and self-contained breathing apparatus.

8. DISPOSAL

Lithium batteries should be returned to stores for disposal. While awaiting disposal, the batteries must be insulated so as to avoid short-circuiting or contact with other batteries. MRL has recommended [17] that discharged lithium-sulphur dioxide batteries be disposed of by scattering the batteries about 2 m apart in a landfill site before being covered. The batteries need not be segregated from other stores. Under no circumstances should batteries be crushed, punctured, or incinerated. Laboratories in the U.S. [18, 19] are examining disposal methods which involve treating the battery's contents with chemicals.

Both the Australian [20] and U.S. [21] Armies are advocating the use of a 'one-time' discharge switch with lithium-sulphur dioxide batteries. This switch completely discharges the battery (to 0.0 V) ensuring that very little lithium or sulphur dioxide remains unreacted. Batteries discharged to 0.0 V are safer to handle and less hazardous to the environment. Attempts [21] are being made to automate this 'one-time' switch. 'One-time' switches cannot be used in conjunction with thionyl chloride based batteries because these batteries produce sulphur dioxide during discharge and do not contain equimolar quantities of thionyl chloride and lithium when first manufactured.

Special care must be taken with damaged batteries. When the battery is safe, the battery terminals must be insulated, the battery or remains placed in a suitable container, and returned to the stores. Damaged batteries should be returned to the manufacturer for inspection or disposed of according to manufacturer's recommendations.

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